



[Document Name] Application for Patent
[Reference No.] 28328
[Application Date] February 9, 2001 (Hei 13)
[Addressee] Commissioner, Patent Office
[International Patent Classification] H01L 21/304
[Title of the Invention]

MICROSTRUCTURE CLEANING METHOD

[Number of Claim(s)] 7
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[Indication of Fee]

[Deposit Account No.] 012472

[Amount of Payment] ¥21,000

[List of Accompanying Document]

[Name of Document] Specification 1

[Name of Document]	Drawings	1
[Name of Document]	Abstract	1
[No. of General Power of Attorney]	9703961	
[Requirements of Proofreading]	Required	



[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION]

MICROSTRUCTURE CLEANING METHOD

[CLAIMS]

[Claim 1] A microstructure cleaning method of removing substances adhering to a microstructure, comprising the step of bringing the microstructure into contact with a high-pressure, fluid of a composite cleaning agent essentially containing carbon dioxide, a detergent agent non-compatible with carbon dioxide, and a compatibilizer.

[Claim 2] The microstructure cleaning method according to claim 1, wherein the carbon dioxide, the detergent agent and the compatibilizer are dissolved in each other in a fluid under a high pressure.

[Claim 3] The microstructure cleaning method according to claim 1, wherein the carbon dioxide, the detergent agent and the compatibilizer are dissolved in each other in an emulsion under a high pressure.

[Claim 4] The microstructure cleaning method according to any one of claims 1 to 3, wherein the detergent agent is a basic substance.

[Claim 5] The microstructure cleaning method according to any one of claims 1 to 4, wherein the basic substance is one of quaternary ammonium hydroxides, quaternary ammonium fluorides, alkylamines, alkanolamines, hydroxylamine and

ammonium fluoride or a compound of some of those.

[Claim 6] The microstructure cleaning method according to any one of claims 1 to 5, wherein the compatibilizer is an alcohol.

[Claim 7] A microstructure cleaned by the microstructure cleaning method according to any one of claims 1 to 6.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of the Invention]

The present invention relates to a method of cleaning a structure having a surface provided with minute irregularities (surface with a microstructure), such as a semiconductor wafer. For example, the present invention relates to a cleaning method of peeling and removing a resist film from a semiconductor wafer in a semiconductor device fabricating process.

[0002]

[Description of the Related Art]

A resist film used for forming a pattern by a semiconductor device fabricating process and unnecessary after the formation of the pattern, and unnecessary, contaminative substances, such as etch residues remaining after etching, must be removed. A wet cleaning method of removing such unnecessary matters from the semiconductor wafer immerses the

semiconductor wafer in a removing liquid, and then rinses the semiconductor wafer with an alcohol or ultrapure water.

[0003]

Although organic and inorganic compounds have been used as removing liquids, recessed parts of a minute pattern cannot be wetted with the removing liquid because of the high surface tension or the high viscosity of the removing liquid, and protruding parts of the minute pattern are destroyed by capillary force produced in gas-liquid interfaces and the volume expansion of the removing liquid and a rinsing liquid during a drying process for drying the removing liquid. Therefore, studies have been made in recent years to use low-viscosity, supercritical carbon dioxide as a removing liquid or a rinsing liquid.

[0004]

Although carbon dioxide serves as a low-viscosity solvent, the dissolving power of carbon dioxide is not insufficient and, when used by itself, the detergency thereof is insufficient. JP-A No. 125644/1998 proposes adding an additive, such as water or methane, or a surface-active agent having CF_x functional groups to the supercritical carbon dioxide. JP-A No. 101963/1996 proposes adding dimethyl sulfoxide or dimethyl formamide to carbon dioxide.

[0005]

The inventors of the present invention made studies and

found that the removing power of a removing liquid prepared by adding the aforesaid additive to carbon dioxide is insufficient for removing a difficult-to-remove resist, such as a phenolic novolac, and there is still room for improvement.

[0006]

A method proposed in JP-A No. 43857/1997 performs a removing process under the normal pressure, using an organic compound and, subsequently, performs a rinsing process using supercritical carbon dioxide. Since the removing process (cleaning process) is performed under the normal pressure, the problem attributable to the insufficient power of wetting minute patterns is not solved.

[0007]

[Problem to be Solved by the Invention]

Accordingly, it is an object of the present invention to find a detergent agent that exhibits high detergency when added to liquid carbon dioxide and to provide a cleaning method having an excellent cleaning effect.

[0008]

[Means for Solving the Problem]

A microstructure cleaning method of removing substances adhering to a microstructure according to the present invention includes the step of bringing the microstructure into contact with a high-pressure fluid of a composite cleaning agent essentially containing carbon dioxide, a detergent

agent noncompatible with carbon dioxide, and a compatibilizer.

[0009]

The cleaning effect is satisfactory when the carbon dioxide, the detergent agent and the compatibilizer are dissolved uniformly in each other in a fluid under a high pressure, or are dissolved in each other in an emulsion under a high pressure.

[0010]

Preferably, the detergent agent is a basic substance. It is particularly preferable that the basic substance is one of quaternary ammonium hydroxides, quaternary ammonium fluorides, alkylamines, alkanolamines, hydroxylamine and ammonium fluoride or a compound of some of those. An alcohol or an alkyl sulfoxide is the most suitable compatibilizer.

[0011]

Preferably, a first rinsing process using carbon dioxide and compatibilizer under a high pressure, and a second rinsing process using only carbon dioxide are performed after the completion of the cleaning process using the composite cleaning agent. The present invention includes a microstructure cleaned by the microstructure cleaning method of the present invention.

[0012]

[Description of the Preferred Embodiments]

A cleaning method according to the present invention is intended to clean a microstructure having minute irregularities, such as a microstructure formed on a semiconductor wafer in a state before the removal of a resist film formed thereon. The present invention is not limited in its application to cleaning such a microstructure formed on a semiconductor wafer, and is applicable to cleaning other objects, such as metal, plastic and ceramic substrates on which a discontinuous or continuous layer of other substances are formed or remain.

[0013]

The cleaning method of the present invention gives consideration to a fact that the detergency of high-pressure carbon dioxide as used by itself is insufficient, and the utmost feature of the cleaning method of the present invention is using a composite cleaning agent containing a detergent agent not compatible with carbon dioxide, and a compatibilizer capable of serving as an auxiliary for uniformly dispersing or dissolving the detergent agent in carbon dioxide in combination with carbon dioxide. High-pressure carbon dioxide is used because high-pressure carbon dioxide has a large diffusion coefficient and is capable of dispersing dissolved contaminants in a medium. Supercritical carbon dioxide has middle properties between those of a gas and those of a liquid and is more capable of permeating a minute pattern

than high-pressure carbon dioxide. The term 'high pressure' as used in this specification signifies a high pressure not lower than 5 MPa. Supercritical carbon dioxide fluid can be obtained at 31°C at a pressure not lower than 7.1 MPa.

[0014]

The detergent agent to be mixed with carbon dioxide may be any compound provided that the compound is insoluble in carbon dioxide and is capable of removing contaminants from a microstructure. Insolubility in carbon dioxide is a requisite because the inventors of the present invention could not have find any compound capable of being dissolved in carbon dioxide, i.e., capable of producing a uniform, transparent mixture together with carbon dioxide, through studies.

[0015]

Preferably, the detergent agent is a basic compound, because basic compounds are expected to be capable of hydrolyzing polymers which are prevalently used as resists. More concretely, the basic compound having a high cleaning ability is, for example, one of quaternary ammonium hydroxides, quaternary ammonium fluorides, alkylamines, alkanolamines, hydroxylamine (NH_2OH) and ammonium fluoride (NH_4F) or a compound of some of those. It is preferable to select one or some of quaternary ammonium hydroxides, quaternary ammonium fluoride, hydroxylamine and ammonium fluoride as a detergent agent when the highest detergency is necessary, such as when

a resist film of a phenolic novolac, which is a difficult-to-remove substance, is to be removed from a semiconductor wafer.

[0016]

Preferable quaternary ammonium hydroxides are, for example, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, and choline ($[\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_3]^+\text{OH}^-$).

[0017]

Preferable quaternary ammonium fluorides are, for example, tetramethylammonium fluoride, tetraethylammonium fluoride, tetrapropylammonium fluoride, tetrabutylammonium fluoride and choline fluoride ($[\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_3]^+\text{F}^-$).

[0018]

Preferable alkylamines are, for example, fatty amines including methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, dipropylamine and tripropylamine. Preferable alkanolamines are, for example, monoethanolamine, diethanolamine and triethanolamine.

[0019]

Preferably, the detergent agent concentration of the composite cleaning agent is 0.01mass% or above, more preferably, 0.05mass% or above. If the detergent agent concentration exceeds 8mass%, the quantity of the com-

patibilizer needs to be increased and, consequently, the quantity of carbon dioxide decreases and the permeation of the composite cleaning agent is reduced. Therefore, it is preferable that the detergent agent concentration is 8mass% or below; more preferably, 6mass% or below, most preferably, 4mass% or below.

[0020]

The detergent agent, either a single substance or a mixture substances, cannot be dissolved in carbon dioxide, and a mixture of the detergent agent and carbon dioxide is divided into a phase of carbon dioxide and that of the detergent agent. Therefore, the composite cleaning agent of the present invention includes essentially the compatibilizer as a third component. The 'compatibilizer' to be used by the present invention is a compound having affinity with both carbon dioxide and the detergent agent and whose existence makes the composite cleaning agent (carbon dioxide, the detergent agent and the compatibilizer), which otherwise is divided into two phases, dissolve uniformly in each other in a fluid or an emulsion under a high pressure. Although it is considered that a uniform, transparent fluid is more permeating into a minute pattern than an emulsion, an emulsion containing particles smaller than intervals between protrusions or the width of recesses in a minute pattern is capable of exhibiting a satisfactory cleaning ability. Therefore, an emulsion may be

used.

[0021]

The compatibilizer may be any agent provided that the agent is capable of compatibilizing a basic substance and carbon dioxide. Alcohols and alkyl sulfoxide are preferable compatibilizers. More concretely, methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and hexafluoroisopropanol are possible compatibilizers. Above all, the compatibilizing function of methanol, ethanol and isopropanol is excellent. Dimethyl sulfoxide is a preferable alkyl sulfoxide.

[0022]

Preferably, the type and quantity of the compatibilizer are determined according to the type and quantity of the detergent agent. A uniform, transparent fluid can be easily prepared when the weight of the compatibilizer is five times that of the detergent agent or above. The quantity of the compatibilizer may be determined so that the compatibilizer concentration of the composite cleaning agent is in the range of 10 to 50mass%. If the compatibilizer concentration exceeds 50mass%, it is possible that the quantity of carbon dioxide decreases and permeation is deteriorated accordingly.

[0023]

The cleaning method using the composite cleaning agent

containing carbon dioxide, the detergent agent and the compatibilizer will be described with reference to the accompanying drawings. Fig. 1 shows a cleaning apparatus in an example for carrying out the cleaning method of the present invention. Shown in Fig. 1 are a carbon dioxide cylinder 1, carbon dioxide feed pump 2, a detergent agent tank 3, a detergent agent feed pump 4, a selector valve 5, a compatibilizer tank 6, a compatibilizer feed pump 7, a selector valve 8, a high-pressure vessel 9, and a thermostatic vessel 10. A workpiece to be cleaned is placed in the high-temperature vessel 9. The carbon dioxide feed pump 2 feeds carbon dioxide from the liquefied carbon dioxide cylinder 1 into the high-pressure vessel 9 and regulates pressure in the high-pressure vessel 9. The thermostatic vessel 10 sets the high-pressure vessel 9 at a predetermined temperature. The thermostatic vessel 10 may be omitted and the high-pressure vessel 9 may be provided with a heating device. Subsequently, the pumps 4 and 7 feed the detergent agent and the compatibilizer from the tanks 3 and 6, respectively, to start the cleaning process. The carbon dioxide, the detergent agent and the compatibilizer may be fed either continuously or in batches.

[0024]

Process temperature for the cleaning process is in the range of 31 to 120°C. The cleaning process takes much time

if the process temperature is below 31°C. Temperatures above 120°C do not improve cleaning efficiency and waste energy. Preferably, process pressure is in the range of 5 to 30 MPa, more preferably, 7.1 to 20 MPa. Process time for cleaning may be properly determined according to the size of the workpiece and the quantity of contaminants. A sufficient process time is in the range of several minutes to several tens minutes.

[0025]

The workpiece cleaned by the cleaning process is subjected to a rinsing process. The rinsing process executes a first rinsing step using a mixture of carbon dioxide and a compatibilizer because foreign matters will be deposited if only carbon dioxide is mixed with a cleaning solution containing a resist and such and remaining on the cleaned workpiece. More concretely, the selector valve 5 is operated to stop feeding the detergent agent, carbon dioxide and compatibilizer are fed into the high-pressure vessel 9, and the solution remaining on the workpiece after cleaning may be discharged from the high-pressure vessel 9 according to feed rate (a flowmeter may be checked). In the rinsing process, it is preferable that the selector valve 8 is operated to decrease the compatibilizer feed rate gradually or stepwise, so that the high-pressure vessel 9 is filled with only carbon dioxide for a second rinsing step, which facilitates drying. A carbon dioxide recovering process processes the liquids used

by the cleaning process and the rinsing process by, for example, a gas-liquid separator to separate the carbon dioxide from liquid components. Thus, the components of the liquids can be recovered and reused.

[0026]

After the completion of the rinsing process, a pressure-regulating valve is operated to set the interior of the high-pressure vessel 9 at a normal pressure. Since carbon dioxide vaporizes substantially instantly, the workpiece, such as a wafer, dries up, spots are not formed on the surface of the workpiece and a minute pattern formed on the workpiece is not destroyed.

[0027]

[Examples]

Examples of the present invention will be described hereinafter. The examples are not limitative and changes within the scope of the present invention are to be considered to be included in the technical scope of the present invention. In the following description, 'part' corresponds to 'part by mass' and '%' corresponds to '% by mass'.

[0028]

Experiment 1

A detergent agent was examined under a normal pressure. A specimen was prepared by forming a SiO_2 film on a Si wafer, coating the SiO_2 film with a resist film of a phenolic novolac,

forming a pattern by subjecting the resist film to a developing process, and forming a minute pattern by dry etching using a fluorine-based gas. The specimen was immersed in a detergent agent shown in Table 1 in a vessel at a temperature in the range of 40 to 100°C (the detergent agent was heated when the resist film was difficult to remove) under a normal pressure for 20 min. In Table 1, crosses and circles indicate that resist removal ratio was below 90% and 90% or above, respectively, when only the detergent agent was used, and double circles indicate that resist removal ratio was 90% or above even when the detergent agent was diluted hundred times with dimethyl sulfoxide or the like. Since ammonium fluoride is solid at an ordinary temperature, a solution containing 1% ammonium fluoride prepared by dissolving ammonium fluoride in a mixed solvent of 1 part water and 9 parts dimethylformamide was used for immersion experiments. Resist removal ratio is the calculated ratio of the area of the surface of the workpiece from which the resist film was removed measured by observation with a microscope to that of the surface of the workpiece initially coated with the resist film measured by observation with the microscope.

[0029]

Table 1

Detergent agent	Cleaning effect
Acetone	×
Dimethylformamide	×
Dimethyl sulfoxide	×
N-methyl-2-pyrrolidone	×
Propylene carbonate	×
Methylamine	○
Ethylamine	○
Monoethanolamine	○
TMAH ^{*1}	⊙
Choline	⊙
Hydroxylamine	⊙
Ammonium fluoride ^{*2}	⊙

*1: Tetramethylammonium hydroxide

*2: Solution containing 1% ammonium fluoride prepared by dissolving ammonium fluoride in a mixed solvent of 1 part water and 9 part dimethylformamide

[0030]

As obvious from Table 1, quaternary ammonium hydroxides, quaternary ammonium fluorides, hydroxylamine and ammonium fluoride exhibited excellent cleaning abilities, and alkylamines and alkanolamines exhibited good cleaning abilities.

[0031]

Experiment 2

An apparatus shown in Fig. 2 was used for examining the effect of compatibilizers. A pump 14 supplied carbon dioxide from a carbon dioxide cylinder 13 into a high-pressure vessel

17 provided with a glass-paned inspection hole 18 to set the interior of the high-pressure vessel 17 at 20 MPa. A thermostatic vessel 19 kept the interior of the high-pressure vessel 17 at 80°C. A pump 16 pumped a mixture of a detergent agent and a compatibilizer mixed in a ratio (concentrations in the high-pressure vessel) shown in Table 2 from a tank 15 into the high-pressure vessel 17. At the same time, a quantity of the carbon dioxide equal to that of the mixture was discharged from the high-pressure vessel 17 to maintain the interior of the high-pressure vessel 17 at 20 MPa. If the carbon dioxide, the detergent agent and the compatibilizer do not dissolved in each other, the carbon dioxide, the detergent agent and the compatibilizer are separated into two phases, i.e., a phase of the carbon dioxide and a phase of the mixture of the detergent agent and the compatibilizer. In Table 2, crosses indicate that the carbon dioxide, the detergent agent and the compatibilizer were separated into the two phases, and circles indicate that the carbon dioxide, the detergent agent and the compatibilizer were not separated into two phases.

[0032]

Table 2

Experiment No.	Detergent agent		Compatibilizer		Compatibility
	Type	Concentration (mass %)	Type	Concentration (mass %)	
1	TMAH*1	1.21	Ethanol	22.1	o
2	TMAH*1	1.50	Dimethyl sulfoxide	30.0	o
3	TBAH*2	0.40	Ethanol	38.1	o
4	Choline	0.05	Ethanol	20.0	o
5	Choline	1.76	Ethanol	35.3	o
6	Choline	0.25	Ethanol	24.0	o
7	Choline	0.29	IPA*3	27.9	o
8	Choline	0.39	DEGMA*4	38.3	o
9	Monoethanolamine	0.05	Ethanol	25.0	o
10	None		None		o
11	None		Ethanol	20.0	o
12	Choline	0.05	None		x

*1: Tetramethylammonium hydroxide,

*3: Isopropanol,

*2: Tetrabutylammonium hydroxide,

*4: Diethylene glycol monomethyl ether

[0033]

As obvious from Table 2, separation of the gases into two phases did not occur when only carbon dioxide was supplied (Experiment No. 10) and when carbon dioxide and the compatibilizer were supplied (Experiment No. 11). The gases were separated into two phases when any compatibilizer was not used (Experiment No. 12). In Experiments Nos. 1 to 9, which conform to the present invention, a transparent, uniform solution could be produced, which verified the effect of the compatibilizer.

[0034]

Experiment 3

The apparatus shown in Fig. 1 was used, and combinations of detergent agents and compatibilizers were used for cleaning specimens prepared for Experiment 1. In Table 3, double circles, circles and crosses indicate that resist removal ratio was 90% or above, 60% or above and 10% or below, respectively.

[0035]

Table 3

Experiment No.	Detergent agent		Compatibilizer		Removing effect
	Type	Concentration (mass%)	Type	Concentration (mass%)	
13	Choline	0.05	Ethanol	20.0	⊙
14	Choline	1.70	Ethanol	35.3	⊙
15	TMAH*1	1.21	Methanol	22.2	⊙
16	TMAH*1	1.50	Dimethyl sulfoxide	30.0	
17	None		None		×
18	None		Ethanol	20.0	×
19	None		Dimethyl sulfoxide	30.0	×

*1: Tetramethylammonium hydroxide

[0036]

Experiments Nos. 13 to 16, which conform to the present invention, could completely remove the resist film. Experiment No. 17 which used only carbon dioxide and experiment No. 18 which did not use any detergent agent left considerably large part of the resist film.

[0037]

[Effect of the Invention]

The cleaning method of the present invention uses the composite cleaning agent containing the detergent agent

noncompatible with carbon dioxide, and a compatibilizer in combination with carbon dioxide, taking into consideration the insufficient detergency of liquid carbon dioxide. Therefore, unnecessary substances adhering to a micro-structure, such as a resist film and an etching polymer remaining on a semiconductor wafer, can be easily removed.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1] Fig 1 is a schematic view of a cleaning apparatus for carrying out a cleaning method in a preferred embodiment according to the present invention.

[Fig. 2] Fig. 2 is a schematic view of a cleaning apparatus used for Experiment 2.

[REFERENCE CHARACTERS]

- 1, 13 Carbon dioxide cylinders
- 2, 14 Carbon dioxide feed pumps
- 3 Detergent agent tank
- 4 detergent agent feed pump
- 5 Selector valve
- 6 Compatibilizer tank
- 7 Compatibilizer feed pump
- 8 Selector valve
- 9, 17 High-pressure vessels
- 10, 19 Thermostatic vessels

- 11 Pressure-regulating valve
- 12 Flowmeter
- 18 Glass-paned inspection hole

[NAME OF DOCUMENT] ABSTRACT

[ABSTRACT]

[OBJECT] Selection of detergent agents capable of exhibiting high detergency when used in combination with liquid carbon dioxide and providing a cleaning method having excellent cleaning effect

[CONSTITUTION] A cleaning method of removing substances adhering to a microstructure comprises the step of bringing the microstructure into contact with a high-pressure, fluid of a composite cleaning agent essentially containing carbon dioxide, a detergent agent noncompatible with carbon dioxide, and a compatibilizer.

[SELECTED DRAWING] Fig. 1